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PROCESS FOR THE MANUFACTURE OF ALVEOLATE CELLULOSIC PRODUCTS
[Procédé de fabrication de produits alvéolaires cellulosiques]

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FOREIGN TITLE (54A): PROCÉDÉ DE FABRICATION DE
PRODUITS ALVÉOLAIRES
CELLULOSIQUES

The invention presently claimed has for its object a new process for the manufacture of alveolate cellulosic products. It likewise concerns those alveolate cellulosic products obtainable by means of said process.

The alveolate cellulosic products are artificial products of the sponge or fabric-sponge type; that is to say, they consist of sponges, fabric-sponges, foam sponges or the like. These materials are utilizable by themselves or integrated into a combined structure, in the domain of hygiene and maintenance, particularly domestic. The term fabric-sponge designates an alveolate cellulosic material comprising two perceptible parallel faces and having little thickness, generally less than a centimeter. The structure of such a material can contain a reinforcing grid.

At the present time, said alveolate cellulosic products are manufactured by a method called the viscose process, well known to the man of art, described in particular in patent FR-A 812,502. This process comprises:

- the preparation of a pasty mass from in particular:

1) a cellulosic solution, such as viscose (said viscose being obtained by the action of an alkaline solution on the paste constituting the cellulosic base, an action that transforms said

*Numbers in the margin indicate pagination in the foreign text.

cellulose paste into alkali-cellulose, which reacts with carbon disulfide to form a cellulose xanthate, a product soluble in sodium water);

2) fibrous materials, such as cotton, sisal and flax, designed to increase the mechanical resistance of the final product;

3) pigments intended to color upon said final product;

4) pore-generating agents, such as Glauber's salt (sodium sulfate decahydrate), soluble and/or fusible crystalline products designed to form pores after coagulation of said pasty mass by lixiviation and/or melting;

- the shaping of this mass by, in particular, molding or coating both sides or one side of at least one grid or deposition on a substrate strip;

- the heating of the same, possibly in a medium adequate for the action of such pore-generating agents, such as regenerated cellulose. This heating can be carried out either by passing an alternating electrical current between electrodes in contact with the paste, or by putting said paste into contact with an acid medium (pH less than 1), at temperatures close to 70 °C, for /2 several minutes (regeneration termed acid, in which a mixture of sulfuric acid and sodium sulfate is advantageously employed, for the fabrication of fabric-sponges), or by contacting said paste into contact with a basic medium (pH close to 12, at temperatures near 100 °C, for several hours (regeneration called basic, in which

a basic solution of sodium sulfate is advantageously utilized for the production of sponges).

The products thus obtained - alveolate cellulose materials - are then, according to the classic method, washed, possibly bleached, dried and plasticized before being cut and packaged.

This process is based upon the chemical modification of the cellulose in the cellulosic base material. (Said cellulose, transformed beforehand into alkali-cellulose, reacts with carbon disulfide to form cellulose xanthate that is soluble in the medium). Said modified cellulose (transformed into one of its derivatives) must be generated at the end of said process. This chemical modification of the cellulose makes use of carbon disulfide. Said carbon disulfide is per se a pollutant. Moreover, it is the source of by-products that are equally polluting: sulfides, polysulfides, thiosulfates, in aqueous solution, hydrogen sulfide in the form of gas.

The implementation of the viscose process therefore result in:

- a pollution of waters by reducing sulfur compounds that give rise to a high chemical demand for oxygen (DCO),
- atmospheric pollution consisting of carbon disulfide, which is assigned to the category of volatile organic compounds (VOC) and hydrogen sulfide, which is malodorous in very low concentrations and generates an undeniable inconvenience for the neighborhood.

Long-term studies have been carried out to reduce these nuisances or bring them under control. Studies have been carried out for the optimization and improvement of the viscose process with a view to minimizing the quantity of carbon disulfide utilized. Thus, in a related field, that for the production of cellulose fibers by spinning viscose, the most advanced companies today prepare the viscose with approximately 28 % of carbon disulfide, relative to the alpha-cellulose employed. Simultaneously, technologies have been developed for the treatment of emissions. The most sophisticated technologies today permit the recycling of all pollutants in aqueous phase and avoidance of any discharge of polluted waters into the natural environment. The technologies for treatment of the gases permit recycling by the adsorption onto active charcoal of up to 70 % of that carbon disulfide utilized for the production of viscose and conversion, /3 by catalytic oxidation, of two thirds of the residual emissions of sulfuric acid, which is itself utilized in the process. The atmospheric emissions can thus be limited today to approximately 10 % of the carbon disulfide employed (these emissions are constituted in part by CS_2 and in part by H_2S). Nevertheless, the techniques employed for keeping pollution problems under control are expensive and endanger the economic viability of the viscose process. That is the reason why research has been conducted since the 1970s for the purpose of developing a new method for the transformation of

cellulose, which does not present the same problems for the environment as the viscose process.

Research has been focused in particular on those methods that do not employ a chemical modification of the cellulose, but employ an intrinsic solvent of the cellulose, thus introducing the economy of transforming the cellulose into one of its derivatives (directly soluble) and of the regeneration of said cellulose from said derivative.

Numerous solvents or solvent systems for cellulose have been discovered or developed and are now known:

- oxides of amines such as N-methyl morpholine N-oxide (NMMO),
- complexes containing a metallic ion, such as cadoxen (cadmium/ethylenediamine/sodium),
- dimethyl sulfoxide (DMSO),
- aqueous solutions of zinc chloride,
- aqueous solutions of zinc chloride,
- mixtures based upon aqueous solutions of lithium chloride,
- aqueous solutions of sodium or of other alkaline hydroxides.

Research on applications of the solution of cellulose obtained have however, until the present day, been focused primarily on the production of artificial cellulose fibers.

Thus, the Asahi Company has made an in-depth study of the aqueous sodium solutions (EP-A 0,147,634), in particular for the production of fibers. This solvent presents evidently the

advantage of being at the same time both inexpensive and nontoxic. However:

- aqueous solutions of sodium do not constitute a very good solvent for cellulose; and to obtain the required dissolution, a pretreatment of the cellulosic raw material was found to be necessary for its activation, for example, by steam bursting;

- the cellulose solutions obtained remain generally turbid /4 and have a tendency to gel. They are consequently difficult to spin.

Only the production of fibers from solutions of cellulose in NMMO is today perfectly under control, notably by Courtaulds, which commercializes fibers, as well as products, under the trademark Tencel®.

Those solvents or solvent systems other than NMMO have thus been the object of more or less thorough development, but have not in any case, to this day, resulted in industrial applications. Certain of said solvents (or solvent systems) have been rapidly abandoned due to cost and/or the toxicity of the solvent itself.

At the present time, to the best of Applicant's knowledge, no company has gained control of an industrial process for the manufacture of alveolate cellulose products, based on a direct dissolution of the cellulose, in an intrinsic solvent of the same. Such a production process presents particular demands that are notably different from those required for the manufacture of

artificial cellulosic fibers. Thus, to the extent that it will not be necessary to employ the cellulosic solution for spinning, it can be *a priori* much less demanding with regard to the quality and homogeneity of said cellulosic solution. On the other hand, to the extent that the intent is to produce a three-dimensional product with a particular porous structure, presenting certain mechanical properties, multiple problems will be encountered.

The porous structure of alveolate cellulosic materials is in fact special, even rather complex, to the extent that, to confer upon said alveolate cellulosic products their remarkable properties of hydrophilia and water-absorption, it presents at the same time both a macro- and a microporosity. Macroporosity - the presence of pores whose size is greater than 100 μm - enables said materials to absorb large quantities of liquid (up to 30 times their own dry weight). Microporosity - the presence of pores of a size less than 10 μm - plays several roles:

- it permits the penetration of liquid into the structure in order to wet the material very rapidly when the latter is dry:

- it assures the circulation of the liquid between the macropores, thus permitting said macropores to be filled and emptied;

- it functions as a check valve providing a seal between the macropores, which permits the latter to retain liquid within themselves so long as the material is not compressed, thus enabling

them to be utilized for the transport of said liquid.

Such a porous structure results, in the viscose process, /5
from the specific action of pore-generating agents, such as
Glauber's salt. The latter, by melting, creates a macroporosity
with dimensions equal to those of the crystals introduced. It thus
plays the role of a coagulant for the viscose, in order to form a
xanthate gel swelled by the sodium. The structure of the gel
prefigures the microporous structure of the finished products. The
exit of carbon disulfide in the form of gas, at the moment of
cellulose regeneration, completes the work of forming the
microporous structure by assuring the opening of the porous
network.

The Applicant has therefore addressed the problem of
developing a nonpolluting method (which does not employ a reactant
such as CS_2 to transform the cellulose into one of its
derivatives), leading to alveolate cellulosic products that present
properties entirely similar to those of alveolate cellulosic
products via the prior art, obtained by the viscose method.

Said process constitutes the first object of the invention
presently claimed.

In a characteristic manner, said process comprises:

- the dissolution, at least partial, of a cellulosic raw
material in an intrinsic cellulose solvent;

- the incorporation, with agitation, into the resulting mixture, of an effective quantity of at least one pore-generating agent, said pore-generating agent or agents compatible with the cellulosic mixture being suitable for the generation of macro- and microporosity when they develop their activity.

- the gelling of the homogeneous pasty mass thus obtained;
- the treatment of said gelled mass under conditions in which the dissolved cellulose precipitates and the action of the pore-generating agent or agents present develops.

Presented below are details concerning each of the above steps. Described, more specifically, are advantageous execution variants.

Within the framework of the invention, since it is not necessary to obtain a total dissolution of the cellulosic raw material (the cellulosic raw material/solvent mixture can consist of a solution, but generally consists of a suspension), the nature of said cellulosic raw material is not critical. Said cellulosic raw material includes, for industrial use of the process, cellulose whose crystalline structure is of the type of cellulose I or cellulose II. The crystallinity rates are a matter of indifference. Advantageously, said starting material will contain cellulose with an average degree of polymerization, evaluated by measuring the viscosity of a solution of said raw cellulosic raw material in cupriethylene diamine, is above 100; in

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a still more advantageous manner, said degree of polymerization is comprised between 200 and 1,000. If the degree of polymerization of that cellulose employed is less than 200, difficulties may be encountered in the effort to obtain final products of quality; if said degree of polymerization of the cellulose employed is in excess of 1,000, difficulties may encountered when attempting to dissolve a sufficient quantity of said cellulose.

As examples of cellulosic materials suitable as raw cellulosic materials for the purpose of implementing the invented process, it is possible to cite:

- wood paste: wood paper pulp or wood pump to be dissolved;
- recycled paper;
- cotton linters;
- cellulose from vegetable waste and, notably, that extract from the parenchyma of the pulp of certain vegetables (such as beets and citrus fruit) or that extract from cereal straw (such as wheat, barley, rye, rice);
- cellulose that has already undergone a transformation (cellulose II) and, notably, that of artificial cellulosic fibers (such as the viscose fibers Fibranne®, Tencel®) or regenerated cellulose articles (such as articles consisting of cellulosic gut, Cellophane® films, sponges). The implementation of the invented process with products of this type ensures the recycling of said

products.

The cellulosic raw material can be utilized, for implementation of the invented process, as is or after having undergone a preliminary treatment designed to render the supramolecular crystalline structure of the cellulose more accessible to the solvent, and to facilitate its dissolution in said solvent.

Such a preliminary treatment is found to be completely superfluous with certain cellulosic raw material/solvent combinations and, in a general way, when NMMO is utilized as the solvent or with celluloses possessing the crystalline structure of cellulose II or cellulose extracts of the parenchyma from the pulp of certain vegetables (such as beets or citrus fruit). Such a preliminary treatment can, on the other hand, be indispensable or highly advantageous with other cellulosic raw material/solvent couples and, in a somewhat general manner, when the aqueous solutions of sodium are utilized as the solvent with the majority of celluloses possessing the crystalline structure of cellulose I and, in particular, wood pulps, cotton linters or natural cellulose fibers. /7

The man of art will know how to appreciate of the opportunity to carry out such a preliminary treatment (to achieve satisfactory rates of dissolution, without however having a negative effect upon the mechanical properties of the final product) and will know how

to control such an implementation. Such a treatment of the cellulosic raw material has in fact been described in other contexts. Said treatments are qualified by activation treatment. They can in particular be carried out according to one or another of the following techniques:

a) Bursting by steam

This activation method was described in particular by the Asahi Company in patent application EP-A 0,147,634. It consists of:

- impregnation of the cellulose with an agent that facilitates the rupture of the intermolecular hydrogen bonds (for example, by water, by an aqueous solution of a salt, by an aqueous solution of an acid, by a basic aqueous solution ...) at the rate of from 10 % to 1,000 % by mass, relative to the dry cellulose,

- the heating of the whole to a temperature comprised between 100 °C and 350 °C, under a pressure comprised between 10 and 250 atmospheres (between approximately 10^6 and $25 \cdot 10^6$ Pa) (the pressure selected can, for example, correspond to the saturating vapor pressure at the temperature in question) for a period of from 20 seconds to 20 minutes,

- abrupt expansion of the whole by the application of atmospheric pressure and ambient temperature.

b) Microfibrillation

This activation procedure is based upon those techniques for refining cellulose employed in the domain of paper. It consists of;

- mixing the cellulosic raw material with water or with a weakly concentrated soda solution (less than 5 % by mass) in order to comprise a pulp comprising dry cellulose in the amount of from 0.1 % to 5 %,

- trituration of the pulp in a homogenizer of the Gaulin type for a period of from 1 to 24 hours.

Said activation treatments, as indicted above, facilitate the dissolution of the cellulose in the solvent. At the level of the structure of said cellulose, they are responsible for a /8 reduction in the length and diameter of the fibers and a reduction in the average degree of polymerization. They thus have an influence upon the mechanical properties of the final product.

As already stated above, the man of art will know how to appreciate the opportunity for their implementation, knowing that, within the context of the invented process, the intent is generally not a total dissolution of the cellulosic raw material in the solvent. The goal is generally not the preparation of a perfect solution, though such preparation is not excluded from the framework of the invention. At the end of the first principal step of the process, the result is generally a cellulosic raw

material/solvent mixture (a suspension); said cellulosic raw material being found, only in part, dissolved in said solvent. Such a mixture is generally utilized as such, in the remainder of the invented process, without separation of the dissolved fraction and the undissolved fraction. The effort is generally made to dissolve at least 30 % by mass of the cellulosic raw material introduced into the solvent, advantageously at least 50 %, said cellulosic raw material having generally been introduced in the amount of from 3 % to 15 % by mass, relative to the mass of the solvent.

The nature of the cellulosic raw material usable within the context of this first dissolution step of the invented process has already been specified above (though it is noted here that, for all useful purposes, mixtures of materials of different types can certainly be suitable) and the advantageously required dissolution rates indicated. Some information on solvents suitable for the purposes of the invention is offered below:

All those chemical compounds known as solvents for cellulose can *a priori* be utilized in the invented process. It will be noted, however, that a selection is made rapidly with a view to their cost, their toxicity, the working conditions under which they are solvents for cellulose, their cost of utilization.

At the present time, the Applicant is advantageously employing aqueous solutions of strong alkaline bases and, in a manner still

more advantageous, aqueous soda solutions. The Applicant recommends, for the implementation of such advantageous variants of the invented process, the utilization of said strong alkaline bases, in aqueous solution, at a concentration comprised between 5 % and 12 % by mass. Recommended, more specifically, is the utilization of aqueous solutions of lithium hydroxide having a concentration of from 5 % to 8 % and the use of aqueous soda /2 solutions having a concentration of from 7 % to 10 %.

Such aqueous solutions of soda are known to be solvents of sodium under the given conditions of temperature: between approximately -15°C and $+10^{\circ}\text{C}$. The literature contains numerous data on tertiary systems: cellulose - soda - water. It is possible to refer in particular to: *Z. physikal. Chem., Abt. B, Bd. 43, Heft 5, pp. 309-328* [*Journal of Physical Chemistry, Dept. B, Vol. 43, No. 5, pp. 309-328*]: "The Cellulose-Sodium Hydroxide-Water system as a Function of Temperature".

According to the invention, the dissolution in such solutions is carried out at temperatures between -15°C and $+10^{\circ}\text{C}$, and preferably between -10°C and 0°C .

A preferred execution variant of the first dissolution step of the invented process is described in detail below, as an illustration:

- an aqueous solution of soda containing, by mass, from 7 to 10 % of soda, preferably from 8 to 9 %, is prepared;

- the cellulosic raw material is preferably coarsely ground by means of a chopping machine;

- the cellulosic raw material can be incorporated into the aqueous soda solution, cooled beforehand, or incorporated into the aqueous soda solution at ambient temperature. In the latter case - the preferred variant - the whole will be cooled together;

- the dissolution is carried out at a temperature comprised between -10°C and 0°C ;

- between 3 % and 15 %, advantageously between 5 and 9 %, of the cellulosic raw material, relative to the aqueous mass of the soda solution, are introduced into the solvent;

- the mixture of cellulose and aqueous soda solution is maintained, with agitation, at the recommended temperature for a period of time of from 30 minutes to 8 hours;

- the agitation is carried out by the use of an agitator with a vertical screw. However, for cellulose concentrations in excess of 7 %, use is made preferably of a malaxator adapted to high-viscosity mixtures, such as, for example, a malaxator with Z arms.

Obtained by this procedure is a cellulosic mixture containing a portion of dissolved cellulose dissolved in an aqueous solution of soda and a portion of undissolved cellulose. Said mixture, without separation of the undissolved portion from the dissolved portion, is utilized later on in the process.

(The solubility rate of the cellulose can be measured in the following manner:

- the cellulosic solution is diluted with an aqueous soda /10 solution having the same concentration as that employed to dissolve the cellulose; this dilution is carried out at ambient temperature. The dilution permits reduction of the cellulose concentration to approximately 1 %;
- the solution obtained is centrifuged at 10,000 rpm for 5 minutes;
- the supernatant solution containing the dissolved portion of the cellulose and the residue containing the undissolved cellulose is then separated.)

In a general way, it is always possible to employ in the mixture (more or less viscous): cellulosic raw material/solvent and additives adapted to facilitate the dissolution of the cellulose. It is thus possible to add, advantageously, from 0.5 % to 5 % by mass of zinc oxide to the aqueous soda solution utilized.

The man of art will know, on the basis of his knowledge and the information given above, how to optimize the nature and the employed quantities of cellulosic raw material and associated solvent in order to obtain a mixture (solution or suspension) in which, in a characteristic manner, pore-generating agents shall be reacted.

The Applicant has succeeded, in a manner by no means obvious, in controlling the application of such pore-generating agents in cellulosic mixtures different from viscose, from which no discharge of CS_2 is evidently anticipated.

The use of pore-generating agents constitutes the second principal step in the invented process. Said pore-generating agents are added to the cellulosic raw material/solvent mixture, with agitation, to generate a pasty homogeneous mass. As will be specified below, other ingredients can be likewise employed in the composition of said pasty mass.

Said pore-generating agents are designed, as already stated, to create the particular porous structure of the finished product, which confers upon said product its properties of hydrophilia and liquid absorption (water...).

The pore-generating agents employed must thus be suitable for the generation of macro- and microporosity within the structure of the finished products (during precipitation of the dissolved cellulose). They must likewise be compatible, obviously, with the cellulosic mixture to which they are added. They must be added to said mixture, in an effective quantity, without inducing consequent coagulation or precipitation of the dissolved cellulose.

Recommended, for implementation of the process according /11 to the invention, is the use of at least one type of pore-generating agent and generally the use of several types of pore-

generating agents. Associated in this second hypothesis with a pore-generating agent called the principal porophore (pore-generating agent) primarily responsible for macroporosity, is at least one pore-generating agent termed the auxiliary porophore, responsible primarily for the microporosity.

By no means excluded however is the use of a single type of porophore or a formulation of pore-generating agents of a type different from that specified above.

Formulations of pore-generating agents suitable for the purposes of the invention can include notably:

- solids capable of melting, sublimating or dissolving,
- solids or liquids capable of liberating gas,
- anionic or cationic polyelectrolytes capable of inducing separation,
- swelling agents that can induce foaming.

The action of the pore-generating agents is quite evidently dependent upon their nature, the conditions of their use and the subsequent conditions of the process.

Recommended notably, for implementation of the invented process, is the use as pore-generating agents of:

- a) at least one solid substance in the form of particles with a granulometry of from 10 μm to 50 μm and, advantageously between 100 μm and 15 μm , which can be activated by melting, sublimation or chemical decomposition. The quantity of this type of agent to be

employed must be calculated on the basis of the total quantity of cellulose contained in the cellulosic mixture (dissolved and undissolved cellulose). Added per 1 part of cellulose are generally from 10 to 100 parts by mass of pore-generating solid, preferably from 20 to 80 parts. As examples of such agents it is possible to cite ice and hydrated salts that can be melted at a temperature below 90 °C, such as, for example, Glauber's salt (sodium sulfate decahydrate: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) or trisodium phosphate dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$);

b) at least one compound chosen among:

+ those solid substances soluble in the cellulosic mixture or insoluble in the same and presenting a granulometry of less than 100 μm and liquids capable of liberating gas over the course of the later steps in the process under the effect of a temperature /12 increase or the action of a chemical agent (for example, acid). The quantity of this type of agent to be used must be calculated as a function of the volume of gas produced relative to the quantity of cellulose employed. Generally from 0.1 mole to 10 moles of pore-generating agent of this type are applied per 100 grams of cellulose.

+ those anionic or cationic polyelectrolytes capable of causing a separation of the cellulosic mixture after its incorporation or over the course of the later stages of the process, under the effect of variations in temperature. Care must

be taken to utilize agents of this type in a neutralized form, because the acid forms are incompatible with the cellulosic mixtures. This type of agent is generally prepared in the form of solutions, particularly aqueous solutions miscible with the cellulosic mixture. The quantity of this type of agent to be used must be calculated relative to the quantity of cellulose solution employed. It will however depend greatly upon the characteristics of the polyelectrolyte, in particular upon the length of the chain and the nature and number of ionic charges. Generally employed are between 0.05 % and 20 % (% by mass) of pore-generating agent of this type, relative to the cellulosic mixture.

+ those swelling agents capable of causing a slight foaming of the cellulosic mixture, either by acting alone or in association with another pore-generating agent. This category includes, in particular, anionic, cationic or nonionic surfactants, the polyols and those products comprising an amide function. This type of agent is generally prepared in the form of solutions, particularly aqueous solutions miscible with the cellulosic mixture. The quantity of this type of agents to be employed within the framework of the invention is to be determined according to the effect of the swelling desired. It is difficult to indicate it in general terms. The incorporation of this type of pore-generating agent into the cellulosic solution induces a slight increase in volume, without however forming a strongly expanded foam.

Those types of pore-generating agents listed above are particularly effective when employed with cellulosic mixtures: cellulosic raw material/aqueous soda solutions.

The Applicant has in particular obtained highly satisfactory results with such mixtures and certain solids of type a) above (solid substances capable of generating a macroporosity and likewise a microporosity to the extent that they are slightly soluble in the cellulosic solution and give rise there to a slight coagulation of the cellulose), with such mixtures and /13 formulations containing solid substances of type a) above and at least one compound of type b) above.

Thus obtained at the end of the first two principal steps in the process according to the invention is a homogeneous pasty mass based upon the cellulosic raw material (at least partially dissolved), the solvent and the pore-generating agent or agents. As indicated above, this pasty mass can contain other ingredients. In fact, according to a preferred execution variant, the invented process will also include, in its first phases, the incorporation of reinforcing fibers and/or additives into the cellulosic raw material/solvent and/or in the pasty mass comprising cellulosic raw material/solvent/pore-generating agent or agents.

The reinforcing fibers are advantageously employed, as in the viscose process, to improve the mechanical properties of the finished product. These can be fibers of any kind:

- natural fibers: wood pulp, cotton, flax, ramie, sisal, hemp, jute, fiber extracts from vegetable waste such as straw;

- artificial fibers: viscose, rayon, Tencel®, cellulose acetate;

- synthetic fibers; polyester, polyamide, polypropylene.

Said reinforcing fibers generally have a length comprised between 0.5 and 50 mm, advantageously, between 1 and 20 mm.

Said reinforcing fibers, when employed, are advantageously added to the cellulosic raw material/solvent mixture before incorporation of the pore-generating agent or agents in order to ensure a good bond between said reinforcing fibers and the dissolved cellulose, to be later precipitated.

It is recalled that the use of said reinforcing fibers is only one possibility. Such an application may be totally superfluous if the cellulosic raw material/solvent mixture already contains, in addition to dissolved cellulose, a sufficient quantity of fibers that have not been dissolved, or if said mixture already includes reinforcing fibers introduced with said cellulosic raw material.

Other additives can be employed opportunely, particularly additives that confer particular properties upon the structure of the finished product, without playing any particular role in the formation of said structure.

It is for example possible, during implementation of the invented process, to incorporate into the cellulosic mixture (or

into the pasty cellulosic mass):

- pigments for coloring the finished product (alveolate /14 cellulosic material, for example, sponge);

- bactericides or fungicides for the protection of said finished product against attack by microorganisms during storage or in the course of its utilization;

- compounds designed to protect said finished product against degradation caused by detergents, lye and, in particular, against that oxidizing degradation induced by solutions of sodium hypochlorite;

- additives designed to prevent the adhesion on or in said finished product of dust, dirt and various types of detritus, which come into contact with said product in the course of its use;

- those products designed to confer upon said finished product greater flexibility in the wet and/or dry state and, in particular, to prevent the hardening of the same when dry or during prolonged storage away from water;

- those compounds that confer greater strength upon said finished product and, in particular, greater resistance to rupture when subjected to traction or torsion and/or greater resistance to abrasion.

It was seen above that chemical compounds can likewise be added to facilitate the dissolution of the cellulose.

Thus obtained via the invented process, at the end of the first two principal steps which include at least partial dissolution of the cellulosic raw material in the solvent and the addition to the obtained mixture of porophores, is a paste or pasty mass constituted by:

- the cellulosic raw material/solvent mixture (where said mixture can consist of a solution but generally consists of a suspension):
- the pore-generating agent or agents;
- optionally, reinforcing fibers;
- optionally, additives.

This paste is prepared by mixing the component ingredients with agitation. It must be homogeneous to produce a final product with a homogeneous structure.

Said paste, homogeneous, is then generally given form according to various methods, known in themselves, as a function of the presentation desired for the final alveolate cellulosic product.

Said paste can be in particular:

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- poured or injected into a mold, with or without the action of compression;
- extruded through a spinner;
- arranged on a support, such as fabric or mesh, or by daubing or by coating using rollers, or by any other method.

According to the invention, in a characteristic fashion, the paste containing the solvent, the cellulose of the dissolved cellulosic raw material, possibly the cellulose of the undissolved cellulosic raw material, the pore-generating agent or agents and possibly at least one additive is gelled. It is not, at the end of its preparation, treated directly to obtain the precipitation of the dissolved cellulose with the conjoint action of the pore-generating agents. It is submitted prior to such treatment to a type of ripening, which was found to be a step indispensable for obtaining a final product with the required properties. This gelling step constitutes a key feature of the invented process. It generally takes place, as stated above, after the formation of said paste.

It is known that the solutions of cellulose exhibit this property of gelling in storage. This was seen to present a problem with regard to spinning them. Gelation is characterized by an increase in the viscosity of the solutions until a gel is obtained, which exhibits, at least in the domain of small constraints and small deformations, the properties of an elastic solid; that is to say, when it is submitted to such constraints (or deformations), said gel does not flow and returns to its original shape when the constraint is relaxed. Said gelation results in an organization of the dissolved cellulose into a structure swelled by the solvent.

Such a gelation can be obtained, under interesting kinetic conditions, by reducing or increasing the temperature of the cellulosic solution and/or by the addition of adequate additives to the same. Such additives can consist in particular of salts or compounds known for their gelling properties. As examples of salts suitable for this purpose, it is possible to cite metallic salts, such as salts of lithium, sodium, potassium, magnesium, calcium, aluminum, manganese, iron, cobalt, nickel, copper or zinc. The salt chosen can be employed in the form of aqueous solution or in crystallized form. The quantity to be utilized, the temperature and the durations of gelation will of course depend upon the /16 salt employed and also upon those properties desired for the gel.

The importance of this gelation phenomenon within the context of implementing the invented process has been confirmed, though somewhat modified, even perturbed by the presence of the pore-generating agents. Its use, which influences the microporosity and mechanical properties, has been optimized by other means.

Supposing the utilization of aqueous solutions of a strong alkaline base and, in particular, of sodium hydroxide, as a solvent, it is recommended that said gelation be carried out at a temperature comprised between -30 °C and +90 °C for a duration of from 1 hour to 400 hours. The procedure for carrying out said gelation according to three advantageous execution variants is the following:

- at ambient temperature, if the pasty mass contains products suitable for gelation within a reasonable time period. Said products can in particular consist of pore-generating agents of the salt type, which dissolve in part in said mass to trigger its gelation, in order to start its coagulation, and/or of gelling agents of the known type (cellulose derivatives, xanthan, starch ...);

- by reducing the temperature to a temperature below -8°C . It is noted that the gel formed when the temperature is raised above -8°C remains stable. In the context of this variant, it is advantageous to work in the following manner: the pasty mass is cooled down to approximately -15°C and then returned to ambient temperature;

- by elevation of the temperature to a temperature above $+30^{\circ}\text{C}$. The temperature selected must remain below that temperature capable of triggering the action of pore-generating agents of the solid type having coarse granulometry and must in any case induce the depolymerization of the dissolved cellulose. It is noted that the gel thus formed is stable and remains so even if the temperature is reduced below $+30^{\circ}\text{C}$.

In a general way, the man of art will know how to optimize this gelation step, in particular, as a function of the nature of the solvent and the pore-generating agents used. It is inspired advantageously by techniques for gelation utilized in procedures

for the manufacture of ultrafiltration membranes.

The gelation of cellulosic solutions not constitute per se an innovative process, as previously noted. The importance of applying an "analogous" gelation to cellulosic solutions /17 charged with pore-generating agents within the context of the preparing alveolate cellulosic materials was however by no means anticipated.

The last principal step in that process according to the invention consists of treating the gelled pasty mass for the purpose of:

- on the one hand of precipitating the greater part or all of that cellulose dissolved in the solvent;
- and
- on the other, triggering the activity of the pore-generating agent or agents to create the final structure of the desired alveolate cellulosic product.

Said last step (applied to the gelled pasty mass at ambient temperature) generally includes several successive or simultaneous steps designed to trigger or even complete the precipitation of the cellulose. Said last step, when a solvent employed consists of NMMO, thus consists of immersing it with the addition of water. In the same way, when the solvent employed is an aqueous solution of at least one strong alkaline base (advantageously an aqueous soda solution), said last step can include the immersion of the gelled

pasty mass, obtained from the preceding steps, in an acid. It is a matter of neutralizing the solvent employed in the course of said immersion. A mineral acid can be utilized for this purpose, such as hydrochloric acid, hydrochlorous acid, sulfuric acid, nitric acid, phosphoric acid, hypophosphorous acid, hydrofluoric acid, hydrobromic acid, or an organic acid such as formic acid, acetic acid, citric acid or oxalic acid. Advantageously, a strong acid is employed at a concentration of from 10 to 100 g/l, at a temperature of from +10 °C to +100 °C, for a time period of from 5 minutes to 8 hours. In a particularly preferred manner, sulfuric acid is utilized. The temperature is not particularly critical, except in that case where this acidification must simultaneously induce the melting of the pore-generating agent or agents. In that case, the treatment temperature must be above the melting temperature of said agent or agents. Such acidification can likewise cause the decomposition of certain types of pore-generating agent, especially those which decompose under the action of an acid to form a gas, for example, the carbonates.

The gelled mass can be submitted to other treatments before or in parallel with such a decisive step. Thus, when the solvent employed consists of an aqueous solution of at least one strong alkaline base, said last step will advantageously include the /18 immersion of the gelled pasty mass in water, at temperature comprised between +40 °C and +100 °C, for a duration of from 5

minutes to 8 hours following its immersion in an advantageously strong acid, as specified above. More generally, said immersion in an advantageously strong acid can be preceded by the one and/or the other of the following steps:

- elevation of the temperature of the gelled pasty mass, without direct contact with a heat-bearing medium: for example, oven-drying, by the use of microwaves, by high-frequency or infrared radiation or via the direct Joule effect in the mass. The purpose of this temperature elevation is either to precipitate the dissolved cellulose, or to melt the pore-generating agent or agents in order to create the porosity. If it is a matter of precipitating the cellulose, the temperature must be raised to at least 60 °C, preferably 70 °C. If it is a matter of melting the pore-generating agent or agents, the temperature must be increased beyond the melting point of the same. Of course, depending upon the pore-generating agent or agents employed, it is possible to induce the precipitation of the cellulose and the melting of said pore-generating agent(s) simultaneously. The duration of such a treatment by elevation of the temperature will depend upon the desired objective and other steps in the final treatment. It can vary between 5 minutes and 12 hours;

- treatment with cold or hot water: the gelled paste can be treated with water by immersion or sprinkling. This treatment can have the purpose either of precipitating the cellulose by washing

out the solvent, or of dissolving the pore-generating agent or agents to create the porosity (or both). These two effects can be combined with a thermal effect analogous to that described in the preceding paragraph in that case where use is made of hot water. The temperature and duration of treatment are adapted to the formulation of the paste and the desired effect;

- treatment with a saline or weakly basic aqueous solution: the gelled paste can be treated with a saline or weakly basic aqueous solution.

Understood by the term saline aqueous solution is an aqueous solution of a soluble salt, for example, a metallic salt of the type of Li, Na, K, Mg, Ca, Al, Mn, Fe, Co, Ni, Cu, Sn. The counterion can be chosen among Cl^- , Br^- , F^- , I^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , CH_3COO^- , PO_4^{3-} , etc.

Understood by the term aqueous weakly basic solution is a basic aqueous solution equivalent to a aqueous soda solution with a concentration below 2 % by mass.

The purpose or purposes of the treatment with a saline or /19 weakly basic aqueous solution, as in the case of the water treatment, can be to precipitate the dissolved cellulose by washing away the solvent and/or to dissolve or melt the pore-generating agents in order to create the porosity. These effects can be combined with a thermal effect in that case where this aqueous solution is hot. The effect of such a treatment is likewise

reinforced by the presence of ion species in solution, which can induce a "salting out" of the dissolved cellulose. This mode of treatment using a saline or weakly basic aqueous solution is particularly adapted to an industrial process, because it permits the recycling of the salt and of the soda, which are recovered in the bath. The temperature and duration of treatment are adapted to the formulation of the paste and the effect desired;

- extraction of the water by evaporation or lyophilization: the gelled paste can be treated under conditions permitting the elimination of the water by evaporation or sublimation. This case, the procedure is preferably carried out under reduced pressure in order to lower the temperature and to avoid a rapid depolymerization of the cellulose. In particular, to effect the sublimation of the water, the procedure is carried out at a temperature below -8°C and a pressure below 6 mbar ($6 \cdot 10^2 \text{ Pa}$). The purpose of extracting the water is to precipitate the cellulose by elimination of the solvent. Extraction with water can contribute simultaneously to the creation of porosity: on the one hand, the departure of the water leaves behind a microporosity in the cellulose phase; on the other hand, if ice or a solid capable of sublimation under analogous conditions is employed as the pore-generating agent, the extraction of the water will create a macroporosity. If this treatment is put into practice, those conditions permitting extraction of the water are generally

maintained until extraction is complete.

Said last step in the invented process can, under certain conditions, be extremely simplified. Thus, particularly when the solvent consists of an aqueous solution of at least one alkaline strong base (advantageously an aqueous soda solution) and the pore-generating agent, single or principal, of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), said last step can consist of simple washing with water. This washing is advantageously implemented first with hot water (for example, in a bath at 90 °C for 1 hour) and then with cold water (for example, in at least one bath at ambient temperature).

Whatever the variant for its execution, this step in the invented process must be lead to the precipitation of a porous mass, the pores resulting from melting, sublimation, /20 dissolution or chemical decomposition of those pore-generating agents present.

At the end of this step, the alveolate cellulosic material has been produced.

It is generally necessary to wash it in order, in particular, to eliminate all traces of those chemical agents utilized to complete the process. This washing is otherwise opportune to the extent that it can permit recovery of such agents and their recycling.

Said washing can be carried out in water, preferably hot water, by immersion or sprinkling for a period of time necessary to achieve the desired degree of purification.

The alveolate cellulosic materials prepared according to the invented process are constituted to 100 % by cellulose, unless:

- synthetic fibers for reinforcement have been introduced into their structure;

or

- additives designed to confer particular properties remain in their structure, being retained physically or chemically.

One part, at least, of the cellulose constituting said materials possess a crystalline structure different from that of cellulose I.

In characteristic fashion, certain materials of the invention include only cellulose whose crystalline structure is of the cellulose II type, to the extent that they were obtained without the use of reinforcing fibers, or where the added reinforcing fibers have had their type I cellulose converting, by use of the solvent, into cellulose of type II.

The alveolate cellulosic materials and particularly sponges prepared by the process according to the invention are characterized by:

- their density;

- their capacity to absorb liquids (water);
- their wettability in the dry state;
- their porous structure;
- their resistance to rupture.

We shall state below the methods for the measurement of these various characteristics and the values obtained with sponges manufactured according to the process of the invention.

- Density

The volume of a sample sponge is determined in the wet state. This sample is oven-dried to obtain a constant mass. The density of the sponge is the mass of the sample in the dry state /21 relative to its volume in the dry state.

The cellulosic sponges obtained by the invented process exhibit a density comprised between 20 and 100 kg/m³.

- The capacity to absorb water

A sponge is immersed in water. It is left there for 5 minutes and then weighed. The mass obtained is then compared with the mass of the same sponge in the dry state.

The cellulosic sponges obtained by the invented process exhibit a capacity to absorb water in an amount 10 times their dry mass.

- Wettability in the dry state

A sponge is dried in the oven to obtain a constant mass. The dry sponge is then placed on the surface of the water and the time

needed for its complete wetting is recorded.

The cellulosic sponges obtained by the process according to the invention exhibit a wettability in the dry state of less than 60 seconds.

- The porous structure

It is shown in those photographs, taken with a scanning electron microscope, attached as figures to the present description.

- The resistance to rupture

A sample of wet sponge with a 20 x 50 mm section (or 10 cm²) is cut up. The resistance to rupture is measured with the aid of a dynamometer. The cellulosic sponges obtained by the invented process exhibit a resistance to rupture in excess of 0.3 daN/cm². Within the context of producing advantageous variants of the invented process, cellulosic sponges were obtained, which present a resistance to rupture clearly in excess of 1 daN/cm²).

In view of the data presented above, the man of art will understand that the Applicant is presently proposing a performing process that constitutes a real alternative to the viscose method.

The invented process makes it possible to obtain, in an industrial manner, alveolate cellulosic products exhibiting properties, in particular, hydrophilia and liquid absorption, entirely similar to those of the alveolate cellulosic products of the prior art, obtained via the viscose methods.

Said alveolate cellulosic products obtained by the process according to the invention are per se novel. Those alveolate cellulosic products obtainable by means of said process therefore constitute the second object of the present invention. /22

Particularly original among said - novel - products are those in which all the cellulose exhibits a crystalline structure consisting of type II cellulose (see above).

The present invention is illustrated by the attached figures and the following example.

Said figures are photographs (with different degrees of enlargement) of the porous structure of a sponge prepared according to the invented process, taken with a scanning electron microscope, the variation of the example being as follows:

The enlargement in Fig. 1 is $\times 35$;

the enlargement in Fig. 2 is $\times 350$;

the enlargement in Fig. 3 is $\times 2,000$.

The presence of macro- and microporosity is seen in these three figures, particularly in Fig. 3.

Example

The cellulosic raw material employed is a dissolved wood pulp obtained by the Kraft process, marketed by International Paper under the trade name Viscokraft HV. This wood pulp possesses a degree of polymerization, measured by the viscosity of a solution in cupriethylene diamine, of 854.

This wood pulp is submitted to an activation treatment by steam bursting under the following conditions;

- impregnation with distilled water for 12 hours,
- exposure to pressure in the presence of water steam at 228 °C, under a pressure of 28 bars ($28 \cdot 10^5$ Pa), for 120 seconds,
- abrupt expansion by exposure to air.

Following this activation treatment, the wood pulp exhibits a degree of polymerization of 422.

The solvent employed in this example is an aqueous soda solution containing 8 % by mass of pure soda.

A solution of cellulose is prepared in said aqueous soda solution in the following manner:

- 5 % by mass of dry cellulose are employed relative to the mass of 8 % aqueous soda solution;

- the wood pulp, utilized in the wet state, is coarsely ground;

- an aqueous soda solution is prepared, taking the /23 humidity of the wood pulp into account, in such a way that the concentration of pure soda following admixture with the wood pulp will be equal to 8 %;

- the aqueous soda solution is cooled to -5 °C;

The aqueous soda solution is mixed with the wood pulp. The mixture is agitated vigorously for 4 hours. The temperature of the mixture is maintained at -5 °C throughout the entire duration of

the agitation.

The cellulosic solution obtained comprises a part of the dissolved cellulose and a part of the undissolved cellulose. It is in fact a suspension. The solubility rate is increased to 70 %.

Reinforcing fibers are then added to said suspension, cotton linters with a length of from 1 to 2 mm being utilized for this purpose. Incorporated are 2 % by mass of these reinforcing fibers, relative to the total mass of the cellulosic suspension. This incorporation is effected by kneading. The temperature of the cellulosic solution thus charged (with the undissolved wood pulp and the reinforcing fibers) is maintained at approximately 0 °C during the course of mixing. Said charged cellulosic solution is then allowed to stand for 1 hour and 30 minutes.

Said cellulosic suspension containing said reinforcing fibers is then mixed with a formulation of pore-generating agents.

Said formulation of pore-generating agents comprises the following two ingredients:

- the principal porophore is sodium sulfate decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. It is employed in crystallized form. The crystals utilized exhibit a distribution of diameters comprised between 100 μm and 3 mm. The quantity of sodium decahydrate employed is 250 % by mass, relative to the mass of charged cellulosic solution;
- sodium lauryl sulfate is employed to induce a slight swelling of the cellulosic solution and to regulate the size of the

microporosity. The quantity employed is 0.5 % by mass of Neopon®, relative to the mass of the charged cellulosic solution.

Said solution of pore-generating agents is mixed with the cellulosic suspension charged with reinforcing fibers by kneading it until a homogeneous paste is obtained. The temperature during the course of kneading is held below 10 °C.

The paste for sponges thus obtained is poured into a mold with the shape of a parallelepiped, with a side length of from 10 to 15 cm. It is then slowly cooled to a temperature of -20 °C, held /24 at this temperature for 24 hours and then returned to ambient temperature in the form of the anticipated gel.

On completion of the gelation step, the paste constitutes a solid gel exhibiting good cohesion, which can be molded without deformation.

The precipitation of the dissolved cellulose and melting of the sodium sulfate is then induced by a treatment in two successive baths:

- hot water at 90 °C for 1 hour;
- cold water (-20 °C) for 8 hours.

The sponge obtained presents an appearance very close to that of a viscose sponge. A surface crust is present, porosity being clearly visible and well formed. It is pliable and elastic in the wet state. It contracts and becomes hard during drying. It becomes wet again virtually instantaneously when dry.

It possesses the following characteristics:

- density (in the wet state): 35 kg/m³ (35 g/dm³)
- water absorption: 17 times its own weight
- resistance to rupture: 0.6 daN/cm².

- Claims -

/25

1. Process for the manufacture of alveolate cellulosic products from a cellulosic raw material, characterized by the fact that it comprises:

- the dissolution, at least partial, of said cellulosic raw material in an intrinsic solvent of cellulose;
- the incorporation into the resulting mixture, with agitation, of an effective quantity of at least one pore-generating agent, said pore-generating agent or agents compatible with the cellulosic mixture, when developing their activity, being capable of the generation of a macro- and a microporosity;
- the gelation of the pasty mass thus obtained;
- the treatment of said gelled mass under conditions where the dissolved cellulose will precipitate and the action of the pore-generating agent or agents is developed.

2. Process according to Claim 1, characterized by the fact that said cellulosic raw material contains cellulose whose crystalline structure is that of the type of cellulose I and/or

cellulose II, and that the degree of average viscosimetric polymerization is above 100, being advantageously comprised between 200 and 1,000.

3. Process according to one of Claims 1 or 2, characterized by the fact that it includes, prior to said at least partial dissolution of said cellulosic material, a treatment for the activation of the same, said activation treatment being based advantageously upon the technique of bursting with steam or the technique of microfibrillation.

4. Process according to any one of Claims 1 through 3, characterized by the fact that, to obtain said at least partial dissolution of said cellulosic material in said intrinsic solvent for cellulose, said solvent is added in the amount of from 3 to 15 % by mass, relative to said cellulosic material.

5. Process according to any one of Claims 1 through 4, characterized by the fact that said cellulosic raw material is dissolved, at least partially, in an aqueous solution of at least one strong alkaline base and, advantageously, in an aqueous soda solution.

6. Process according to Claim 5, characterized by the fact that the dissolution is carried out at a temperature comprised between -15°C and $+10^{\circ}\text{C}$, in a solution containing from 5 to 12 % by mass of said strong base or bases.

7. Process according to any one of Claims 1 through 6, /26
characterized by the fact that it includes the incorporation, as a pore-generating agent, of at least one solid in the form of particles with a granulometry comprised between 10 μ m and 50 μ m, and advantageously between 100 μ m and 15 μ m, and that the solid is activated by melting, sublimation, dissolution or chemical decomposition.

8. Process according to any one of Claims 1 through 17, characterized by the fact that it includes the incorporation, as a pore-generating agent, at least one compound selected among:

- those solids soluble in the cellulosic mixture, or insoluble in the same, and presenting a granulometry below 100 μ m and liquids capable of liberating a gas in the course of several later steps of the process, under the effect of an increase in temperature or under the action of a chemical agent;

- those anionic or cationic polyelectrolytes capable of inducing an unmixing of the cellulosic mixture, after their incorporation or over the course of later steps in the process, under the effect of temperature variations;

- those swelling agents capable of inducing a slight foaming of the cellulosic mixture.

9. Process according to any one of the preceding Claims 1 through 8, characterized by the fact that it includes the incorporation of reinforcing fibers and/or of additives into

cellulosic raw material/solvent mixture and/or into the pasty mass consisting of cellulosic raw material/solvent/pore-generating agents.

10. Process according to any one of Claims 1 through 9, characterized by the fact that the homogeneous pasty mass, advantageously formed, is gelled at a temperature comprised between -30°C and $+90^{\circ}\text{C}$ for a duration of from 1 hour to 400 hours.

11. Process according to any one of Claims 5 through 10, characterized by the fact that the treatment of the gelled mass includes the immersion of the same in an acid solution or washing with water.

12. Alveolate cellulosic products that can be obtained by a process according to any one of the preceding claims.

13. Alveolate products according to Claim 12, in which all the cellulose exhibits a crystalline structure of the type of cellulose II.

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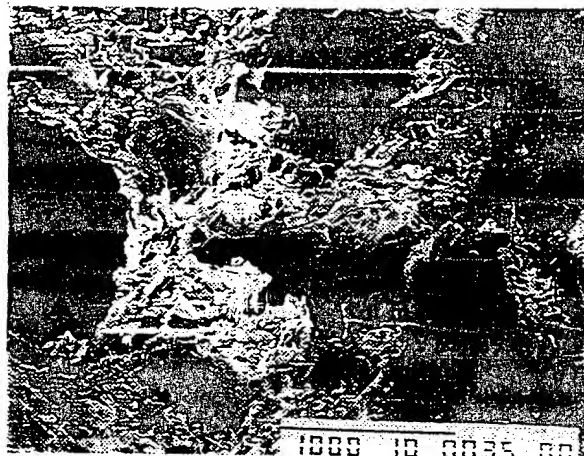
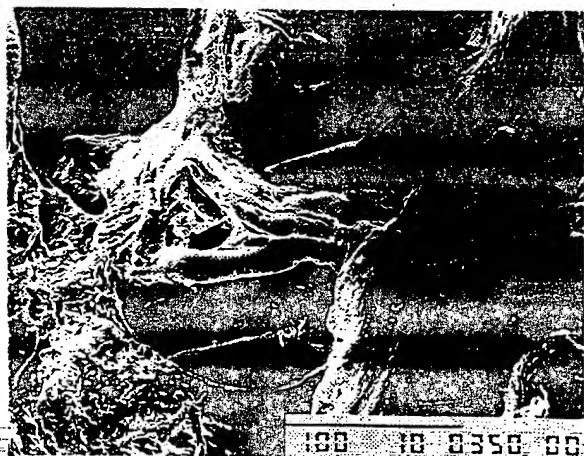
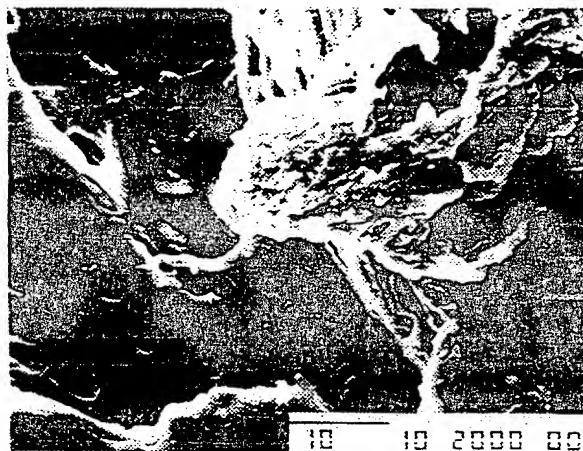


FIG. 1



2/2



FIG_3